

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**First-principles study of photoinduced electron-transfer dynamics in a Mg-porphyrin-quinone complex**

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/137602> since 2016-11-21T12:23:46Z

*Published version:*

DOI:10.1016/j.cplett.2010.08.072

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in CHEMICAL PHYSICS LETTERS, 498, 2010, 10.1016/j.cplett.2010.08.072.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), 10.1016/j.cplett.2010.08.072

The publisher's version is available at:

<http://linkinghub.elsevier.com/retrieve/pii/S0009261410011784>

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/2318/137602>

# First-principles study of photoinduced electron-transfer dynamics in a Mg-porphyrin-quinone complex

Raffaele Borrelli<sup>a,b</sup>, Wolfgang Domcke<sup>a</sup>

<sup>a</sup>*Department of Chemistry, Technische Universität München, D-85747 Garching, Germany*

<sup>b</sup>*Department of Chemistry, University of Salerno, I-84084 Fisciano, Italy*

---

## Abstract

The photoinduced electron-transfer process between a magnesium-porphyrin and a quinone in a model complex has been studied by means of quantum dynamical methods. The microscopic parameters controlling the electron-transfer process have been obtained using *ab initio* electronic structure calculations. A quantum dynamical simulation for a reduced dimensionality model, including only the totally symmetric vibrational degrees of freedom of the quinone molecule, shows that the electron-transfer is fast, taking place in a few hundreds of femtoseconds, in agreement with experimental results for similar systems.

---

## 1. Introduction

Photoinduced electron-transfer (ET) reactions are the basic processes of solar energy conversion both in living systems and in artificial molecular machines.[1, 2] In the past decades, a large variety of model systems have been experimentally investigated with the aim of understanding the detailed molecular mechanisms of such processes. Amongst others, supramolecular complexes consisting of porphyrin-type or phtalocyanine-type electron donors and quinone-type electron acceptors have been widely used, mainly as simplified models of the primary charge-separation process which takes place in biological systems. The rates of ET in such systems can vary from a few hundred femtoseconds a few hundred picoseconds depending on the relative orientation and distance of the molecules, their electron affinities, ionization potentials, and the properties of the medium in which the reaction takes places.[2] Recently, Sobolewski and Domcke have shown that by introducing

a chain of hydrogen-bonded water molecules, which hold together a porphyrin donor and a quinone acceptor, it is possible to trigger a sequence of photoinduced electron-driven proton-transfer (EDPT) reactions, which ultimately lead to splitting of water into hydrogen and oxygen, thus producing a chemical fuel directly using solar energy.[3, 4]

Understanding the mechanistic aspects of ET in such models can be of great importance for the design of new molecular devices capable of producing solar fuels. In particular, a better understanding of the role played by intramolecular and intermolecular vibrations as well as by the solvent is essential. This requires the development and assessment of theoretical models based on a microscopic description of the electronic and nuclear properties of the electron donor-acceptor pair. A full microscopic description of ET reactions is quite challenging even for simple donor-acceptor pair systems, and, notwithstanding the evolution of methodologies for studying exact quantum dynamics in large systems,[5] applications to ET reactions of chemical interest are at an early stage.[6, 7, 8, 9, 10, 11]

In this paper, we discuss a model Hamiltonian of photoinduced ET in a porphyrin-quinone complex and provide preliminary results on the quantum dynamics of the ET process. In particular, we determine the microscopic parameters which control the nuclear motion in the photoinduced ET reaction using high-level electronic structure calculations, and apply wavepacket propagation methods to study its dynamical aspects. Our attention is mainly focused on the role played by the intramolecular vibrations, deliberately neglecting the effect of the surrounding medium and of any low frequency intermolecular motion, with the purpose of understanding to what extent the intramolecular vibrational modes of the two redox partners can drive long-range ET, and which of these are the most effective.

The structure of the complex considered in this work is shown in figure 1. The planes of the two molecules are perpendicular to each other with overall  $C_s$  symmetry. The minimum atom-atom distance is about 4.5 Å, whereas the center-to-center distance of the two rings is about 6.5 Å. The model adopted in this work is based on that proposed in Ref. [3]. The rationale behind this choice is to allow an easy extension of the present calculations to the more complex case of ET reactions coupled to water oxidation processes, which will be the subject of future research. We would like to emphasize that although the arrangement of the donor-acceptor pair in the complex definitely influences the ET rate, most of the analysis presented in this paper remains valid for a large class of porphyrin-quinone complexes, independently from

the mutual orientation of the two moieties (*vide infra*).

INSERT FIGURE 1

## 2. Electronic-Structure Computations

ET in a weakly interacting donor-acceptor pair is most conveniently described as a transition between two diabatic electronic states, corresponding to reactants and products, respectively. A widely employed strategy for determining diabatic states is based on the concept of maximizing the overlap of the electronic wavefunctions with reference diabatic states, which have been defined using some specific property of the system, or by chemico-physical intuition. In this work, an *ab initio* quasi-diabatization procedure has been implemented. In this procedure, the electronic eigenstates,  $\{\Phi_i^o\}$ , of the porphyrin-quinone pair at a very large distance (about 50 Å), *i.e.* with a vanishingly small interaction, are computed and taken as reference diabatic states. Then, the porphyrin-quinone intermolecular distance is changed to the value of interest, in our case 4.5 Å, and a new set,  $\{\Phi_i\}$ , of adiabatic electronic eigenstates is computed. Finally, diabatic states,  $\{\Psi_i\}$ , are obtained by a unitary transformation of the adiabatic states,  $\{\Phi_i\}$ . The unitary transformation is determined by maximizing the overlap,  $\langle\Psi_i|\Phi_i^o\rangle$ , between the diabatic wavefunctions and the reference states. The technique used for the overlap maximization is described in detail in ref [12] and [13] and implemented in the Molpro software.[14] Once the unitary transformation is determined, the adiabatic electronic Hamiltonian can be easily transformed to the diabatic Hamiltonian, providing the energies and the the diabatic coupling matrix element which is responsible for the ET process.

Electronic states have been computed using a state-averaged multi-configuration self-consistent field (SA-MCSCF) method, with the standard Dunning cc-pVTZ basis set.[15] The active space of the MCSCF calculations includes six orbitals localized on the Mg-porphyrin and three orbitals localized on the benzoquinone.

The results of the MCSCF calculations show that the Mg-porphyrin-benzoquinone complex has two quasi-degenerate locally-excited states of  $A'$  and  $A''$  symmetry, which correlate with the  $B_{3u}$  and  $B_{2u}$  excited singlets of the isolated Mg-porphyrin. The  $A'$  state has a slightly lower excitation energy than the  $A''$  state. The lowest CT state can be described almost exclusively as a single excitation from the highest occupied orbital of the Mg-porphyrin

to the lowest unoccupied orbital of benzoquinone, and belongs to the  $A'$  symmetry representation.

Since the transformation to the diabatic representation preserves the symmetry of the electronic wavefunctions, a purely electronic diabatic coupling between the CT state and the  $A'$  locally-excited state is allowed, whereas the CT state and the  $A''$  excited state can only be coupled through a motion along a vibrational mode with  $a''$  symmetry. In this latter case the interaction between the two states would be mediated by a conical intersection (CI). Although it has been pointed out that CIs can significantly influence the ET dynamics,[16, 17] a purely electronic coupling is very effective in driving long-range ET processes, and is a widely used approximation for the study of ET in systems of biochemical interest. Accordingly, we take into account only the possibility of ET from the  $A'$  excited state which is believed to play the major role. Work is currently in progress to include the effect of the  $A''$  excited state. Excitation energies have also been computed at the CC2 level with a split-valence basis set (SVP). The results are summarized in Table 3.

Equilibrium structures, normal vibrations and frequencies of porphyrin and the porphyrin cation in their ground electronic states have been computed in  $D_{4h}$  symmetry, with density functional theory (DFT), using the hybrid B3LYP exchange-correlation functional,[18, 19] and the 6-311G(d,p) basis set, whereas those of quinone and the quinone anion have been computed in  $D_{2h}$  symmetry at the CC2 level, using a cc-pVTZ basis set augmented with diffuse functions (aug-cc-pVTZ).[15] DFT calculations have been performed using the Gaussian09 package,[20] and CC2 calculations have been performed with the Turbomole software[21, 22]. Linear and quadratic vibronic coupling parameters and Duschinsky transformations (*vide infra*) have been computed using a modified version of the MolFC software.[23, 24]

### 3. Model Hamiltonian for Porphyrin-Quinone ET

Electronic-structure analysis show that the dynamics of the photoinduced ET process in porphyrin-quinone complexes can be described by the following diabatic model Hamiltonian

$$H = |P^*Q\rangle(T+U^e)\langle P^*Q| + |P^+Q^-\rangle(T+U^{ct})\langle P^+Q^-| + V|P^*Q\rangle\langle P^+Q^-| + c.c. \quad (1)$$

where  $|P^*Q\rangle$  denotes the locally-excited state of the complex, *i.e.* in which the porphyrin is in its first excited singlet state ( $S_1$ ), and the quinone in

its ground state,  $|P^+Q^- \rangle$  is the charge transfer state,  $U^e$  and  $U^{ct}$  are their respective potential-energy surfaces (PES),  $T$  is the nuclear kinetic-energy operator, and  $V$  the diabatic electronic coupling. In the specific case under examination, both the diabatic locally-excited state and the CT state belong to the  $A'$  symmetry. In this work, we deliberately neglect any intermolecular motion, and further assume that the PESs of the diabatic electronic states can be written as the sum of the PESs of the two separate molecules. Finally, the harmonic approximation is employed. Using the normal-mode representation, we can write the PESs of the two diabatic states as

$$U^e = \frac{1}{2} \sum_i \omega_{Pi} q_{Pi}^2 + \frac{1}{2} \sum_j \omega_{Qj} q_{Qj}^2 \quad (2)$$

$$U^{ct} = \frac{1}{2} \sum_i \tilde{\omega}_{Pi} \tilde{q}_{Pi}^2 + \frac{1}{2} \sum_j \tilde{\omega}_{Qj} \tilde{q}_{Qj}^2 + \Delta E^\circ \quad (3)$$

where  $q_{Qj}, \omega_{Qi}$  are the dimensionless normal coordinates and frequencies of benzoquinone in its ground state, and  $q_{Pi}, \omega_{Pi}$  those of porphyrin in its first excited state. Analogously,  $\tilde{q}_{Qj}, \tilde{\omega}_{Qj}$ , and  $\tilde{q}_{Pi}, \tilde{\omega}_{Pi}$ , are the normal vibrations and frequencies of the benzoquinone radical anion,  $Q^-$ , and of the porphyrin radical cation,  $P^+$ .  $\Delta E^\circ$  is the driving force of the ET.

For computational purposes, it is often better to write the two PESs in terms of the same set of variables.[25] To this end, a Duschinsky transformation can be used to express the normal modes of the CT state in terms of those of the initial electronic state

$$\tilde{q}_P = J_P q_P + d_P, \quad \tilde{q}_Q = J_Q q_Q + d_Q, \quad (4)$$

where the vectors  $d_P, d_Q$  represent the displacements of the equilibrium positions of the normal modes of vibration upon ET, and the linear transformation matrices  $J_P, J_Q$  (the so called Duschinsky matrices) account for variations of directions and frequencies of normal modes. Then, by substituting equations (4) in equation (3), we obtain the transformed PES of the CT state

$$U^{ct} = \Delta E_v + \sum_i \kappa_i^P q_{Pi} + \sum_{i>j} \gamma_{ij}^P q_{Pi} q_{Pj} + \sum_i \kappa_i^Q q_{Qi} + \sum_{i>j} \gamma_{ij}^Q q_{Qi} q_{Qj}, \quad (5)$$

where the linear vibronic couplings  $\kappa_i^{\{P,Q\}}$ , and the Hessian matrices  $\gamma_{ij}^{\{P,Q\}}$

are defined as

$$\kappa_i^P = \tilde{\omega}_{Pi} \sum_j J_{Pij} d_{Pj} \quad \kappa_i^Q = \tilde{\omega}_{Qi} \sum_j J_{Qij} d_{Qj} \quad (6)$$

$$\gamma_{ij}^P = \sum_k J_{Pik} \tilde{\omega}_{Pk} J_{Pkj} \quad \gamma_{ij}^Q = \sum_k J_{Qik} \tilde{\omega}_{Qk} J_{Qkj}. \quad (7)$$

$$\Delta E_v = \Delta E^\circ + \lambda_Q + \lambda_P \quad (8)$$

and  $\lambda_P, \lambda_Q$  are the reorganization energies of porphyrin and benzoquinone respectively, defined as

$$\lambda_P = \frac{1}{2} \sum_i d_{Pi}^2 \tilde{\omega}_{Pi}, \quad \lambda_Q = \frac{1}{2} \sum_i d_{Qi}^2 \tilde{\omega}_{Qi}.$$

$\Delta E_v$  represents the vertical energy difference between two electronic states, *i.e.* computed at the equilibrium geometry of the initial state. The linear vibronic terms depend on the changes of the equilibrium geometries of the molecules upon ET. Second-order terms depend only on the mixing of normal modes, *i.e.* on the Duschinsky effect.

Finally, in the model under examination, the diabatic electronic coupling,  $V$ , is approximated to be independent of the nuclear coordinates. This is an ubiquitous assumption in the theory of ET reactions, which can be safely applied here since, as already pointed out, both the excited state and the CT state belong to the  $A'$  symmetry representation, thus allowing for a purely electronic coupling term.

#### 4. Model Parameters

In order to determine the parameters of the model Hamiltonian, the normal vibrations of Mg-porphyrin in its first excited singlet state and of its cation, as well as of benzoquinone and its anion must be determined. Low-temperature electronic spectra of metalloporphyrins show that in the Q band (*i.e.* in the  $S_1$  state) the 0-0 excitation carries a very large fraction of the total intensity.[26, 27] This suggests that the equilibrium geometries and normal modes of Mg-porphyrin in the first excited state and in the ground state can be assumed to be identical without significant loss of accuracy. This approximation allows us to strongly reduce the computational cost by avoiding the expensive calculation of the excited-state normal vibrations. Computational details of the normal-mode calculations are reported in Section 2.



The totally symmetric modes of the two molecules play a major role in ET as they give rise to linear vibrational couplings,  $\kappa_i$ , which can efficiently drive the ET process. Non-totally symmetric modes, on the other hand, contribute to the Hamiltonian only through quadratic vibronic couplings,  $\gamma_{ij}$ , providing a less efficient mechanism for energy transfer from electronic to nuclear degrees of freedom. The computed  $\kappa_i$  values for the totally symmetric modes of porphyrin and benzoquinone are reported in Table 2. High-frequency ( $\omega > 3000 \text{ cm}^{-1}$ ) totally symmetric modes, which are mainly combinations of CH stretchings, have a very low vibronic activity, and their contribution to the reorganization energy is negligible and not reported. The computed reorganization energy for reduction of benzoquinone ( $\text{Q}/\text{Q}^-$ ) is  $3557 \text{ cm}^{-1}$ , whereas that of the oxidation of Mg-porphyrin ( $\text{P}/\text{P}^+$ ) is  $771 \text{ cm}^{-1}$ . Thus, the overall reorganization energy is  $4328 \text{ cm}^{-1}$ , about 0.54 eV, in surprisingly good agreement with values obtained from the measurement of ET kinetics in cyclophane-bridged porphyrin-quinone molecules.[28] It is worth noting that more than 80% of the total reorganization energy of the system can be ascribed to just five vibrational modes of benzoquinone. These modes are sketched in figure 2. Their strong vibronic activity is ultimately caused by large variations of the benzoquinone geometry upon electron uptake. In particular, the computed geometries predict an elongation of the CO and CC bonds of about 0.06 and 0.04 Å, respectively, and an overall squeezing of the six-membered ring. The elongation of the two bonds can be explained considering that most of the excess electronic charge of the anion is located on the two CO bonds, causing their weakening. This also explains the variation of the vibrational frequency of the symmetric CO stretching upon reduction, as reported in figure 2. Changes in the other geometric parameters do not have such an immediate interpretation. In Table 1, the Hessian matrix,  $\gamma_{ij}^Q$ , for the five totally symmetric modes of benzoquinone is also reported. The strong coupling between modes  $\nu_2, \nu_4, \nu_5$  are due to significant variations of normal modes upon ET.

The vibronic activity of the Mg-porphyrin in the oxidation process is quite complex to analyze. As is well known, the minimum-energy structure of the ground state of Mg-porphyrin exhibits  $D_{4h}$  symmetry, whereas its cation has a lower symmetry ( $C_{4h}$ ). Indeed, both experiments and computations predict an in-plane distortion of the porphyrinic ring of the cation along an  $a_{2g}$  mode ( $a_g$  in the  $C_{4h}$  group).[29, 30, 31] This distortion is caused by a pseudo Jahn-Teller (JT) interaction between the two lowest doublet states of the cation, labeled as  $^2A_{2u}$  and  $^2A_{1u}$  in the  $D_{4h}$  group. In this work, we do not investigate

the role of this pseudo-JT effect on the ET process, and assume that only the lowest doublet state of the porphyrin cation, *i.e.* the  ${}^2A_{2u}$  state, is involved in the reaction. Further work is certainly required along this direction. The in-plane distortion falls at  $1375\text{ cm}^{-1}$  in the neutral porphyrin, and, as can be seen from Table 2, has a relatively strong vibronic activity. The computed reorganization energy of porphyrin is about  $771\text{ cm}^{-1}$ , which clearly indicates that the overall vibronic activity of the molecule is quite small compared to that of benzoquinone.

The vertical energy difference  $\Delta E_v$  is a very important parameter for ET dynamics, as it controls the density of vibronic states which are actually involved in the ET dynamics. Calculation of this parameter for the system of Figure 1 at the CC2 level with a TZVP basis set gives a value of about 1.0 eV. From equation 6, and considering the computed reorganization energies, the ET process would be endoergonic by about 0.5 eV and thus would not take place in the isolated system. On the other hand, the main purpose of our analysis is the description of the ET process in condensed phase, where the stabilization of the CT state due to solvent polarization can be quite significant.[2] Furthermore, the driving force of the ET can be adjusted by introducing specific substituents on the porphyrin or quinone rings. This would not significantly alter the dynamical properties of the system, leaving the present analysis valid.[2, 32] In this work, we assume  $\Delta E_v = 0$ , which amounts to modeling a barrierless ET process with a driving force  $-\Delta E^\circ = \lambda_Q + \lambda_P$  of about 0.5 eV. This assumption, albeit *ad hoc*, has a sound physical basis, as barrierless ETs have been widely documented in porphyrin-quinone type complexes.[2, 28]

The diabatic coupling,  $V$ , between the excited state,  $|P^*Q\rangle$ , and the CT state,  $|P^+Q^-\rangle$ , computed by the diabaticization procedure explained in section 2, is  $120\text{ cm}^{-1}$ . Empirical estimates based on Marcus theory of ET in metallo-porphyrin-quinone systems with a similar edge-to-edge distance suggest values between  $100\text{-}160\text{ cm}^{-1}$ , and similar values can be obtained using the Hopfield semiempirical formula.[33]

## 5. Electron-transfer dynamics

The model Hamiltonian described above has more than hundred vibrational degrees of freedom. A complete numerical treatment of the nonadiabatic dynamics is currently being addressed by using the ML-MCTDH method.[5, 34, 35] However, since more than 80% of the reorganization en-

ergy arises from the five vibrations of the quinone, a reduced-dimensionality model including only these modes should provide a qualitatively correct picture of the ET dynamics. Due to the relatively high frequency of the benzoquinone vibrations, we can neglect any temperature effects and can assume that the system is initially in its vibrational ground state  $|\bar{0}\rangle$ . Then, the vibronic state of the system at any time  $t$  is given by

$$|\Psi(t)\rangle\rangle = e^{-iH_r t/\hbar} |P^*Q\rangle |\bar{0}\rangle, \quad (9)$$

where  $H_r$  is the diabatic reduced Hamiltonian, including only linear and quadratic vibronic couplings of benzoquinone. The time evolution of the wavepacket is computed using a Chebyshev propagator, combined with a grid representation of the vibrational wavefunction.[36] The survival probability as a function of time can be readily obtained from  $|\Psi(t)\rangle\rangle$ :

$$P(t) = \sum_v \langle \bar{v} | \langle P^*Q | \Psi(t) \rangle\rangle \quad (10)$$

where the summation is over all the vibrational states. The ET probability is given by  $1 - P(t)$ .

In Figure 3, the electronic population dynamics of the photoinduced ET process is shown. The system is initially found in the  $|P^*Q\rangle$  electronic state whose population decays rapidly, reaching a value of about 0.2 in about 200 fs, which implies that the CT state is populated on the same timescale.  $P(t)$  exhibits damped oscillations up to 2 ps. The recurrences are most likely due to the limited number of degrees of freedom of our model thus allowing transient back-transfer of the electronic population.

The results of the dynamics are in qualitative agreement with experimental data on porphyrin-quinone complexes having similar structural parameters. In particular, we note that in cyclophane-bridged Zn-porphyrin-quinone[28, 37], ET kinetic constants between  $3 \times 10^{12}$  and  $5 \times 10^{12}$  have been measured, which corresponds to exponential decay times between 330 and 250 fs. In these cases, the estimated diabatic coupling was around 100  $\text{cm}^{-1}$ , and the ET process was considered barrierless, which is in close correspondence with the main features of our *ab initio* based model.

## 6. Conclusions

We have developed an *ab initio* microscopic model of the photoinduced ET process in a Mg-porphyrin-benzoquinone complex employing accurate

electronic structure calculations. Our analysis shows that most of the vibronic activity during the ET reaction is associated with nuclear motion in the benzoquinone anion. This is due to large changes of the molecular geometry upon reduction of benzoquinone. The computed intramolecular reorganization energy is in good agreement with experimental estimates for similar molecular systems. A reduced-dimensionality model, including the five most active accepting modes of benzoquinone, has been used to simulate the ET dynamics. The only empirical parameter is the vertical energy difference  $\Delta E_v$  which has been set to zero to account implicitly for the stabilization of the CT state due to the solvent.

The results show that the ET is very fast and takes place on a subpicosecond timescale, in line with experimental findings on systems with similar structural parameters. This also shows that five intramolecular modes of the redox partners are sufficient to efficiently drive the ET, a most important result for quantum dynamical modeling of chemical processes in large molecular systems. Accurate quantum dynamical simulations including all the degrees of freedom of the system are currently being studied using more powerful quantum dynamical methods. The present model does not include nonequilibrium solvation effects, *i.e.* solvent reorganization. Although these effects clearly contribute to the ET reaction, we expect them to play a minor role for the short-time dynamics of the system (*i.e.* the first few hundred femtoseconds). They may have a deeper impact on the long-time behaviour, leaving our main conclusions unaffected.

It should be noted that our model includes the dynamical effects of both equilibrium geometry changes and normal mode mixings (Duschinsky rotations) upon ET. The latter effect is often neglected in vibronic models, because it is quite difficult to be reliably computed and because it is believed to play a secondary role in the overall dynamics. However, recent theoretical analyses have shown that Duschinsky rotations can have a strong effect on ET rates.[38, 39, 40, 41, 42]

## Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) through a research grant and through the DFG Cluster of Excellence “Munich Centre for Advanced Photonics” ([www.munich-photonics.de](http://www.munich-photonics.de)).

## References

- [1] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737.
- [2] M. R. Wasielewski, *Chem. Rev.* 92 (1992) 435.
- [3] A. L. Sobolewski, W. Domcke, *J. Phys. Chem. A* 112 (2008) 7311.
- [4] A. L. Sobolewski, W. Domcke, *Chem. Phys. Lett.* 409 (2009) 144-.
- [5] H. Wang, M. Thoss, W. H. Miller, *J. Chem. Phys.* 115 (2001) 2979.
- [6] R. Borrelli, M. Di Donato, A. Peluso, *Biophys. J.* 89 (2005) 830.
- [7] R. Borrelli, M. Di Donato, A. Peluso, *Theor. Chem. Acc.* 117 (2007) 957.
- [8] W. W. Parson, A. Warshel, *J. Phys. Chem. B* 108 (2004) 10474.
- [9] M. Thoss, I. Kondov, H. Wang, *Phys. Rev. B: Condens. Matter Mater. Phys.* 76 (2007) 153313.
- [10] M. Thoss, I. Kondov, H. Wang, *Chem. Phys.* 304 (2004) 169.
- [11] I. Kondov, M. Thoss, H. Wang, *J. Phys. Chem. A* 110 (2006) 1364.
- [12] D. Simah, B. Hartke, H. Werner, *J. Chem. Phys.* 111 (1999) 4523.
- [13] W. Domcke, C. Woywod, M. Stengle, *Chem. Phys. Lett.* 226 (1994) 257.
- [14] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, et al., *Molpro*, version 2008.2, a package of ab initio programs, see <http://www.molpro.net> (2008).
- [15] T. H. Dunning, *J. Chem. Phys.* 55 (1971) 716.
- [16] G. A. Worth, L. S. Cederbaum, *Chem. Phys. Lett.* 338 (2001) 219.
- [17] G. Olaso-Gonzalez, M. Merchan, L. Serrano-Andres, *J. Phys. Chem. B* 110 (2006) 24734.
- [18] A. D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [19] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 37 (1988) 785.

- [20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. R. *et al.*, Gaussian 09 Revision A.1, gaussian Inc. Wallingford CT 2009.
- [21] TURBOMOLE V6.1 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from <http://www.turbomole.com>.
- [22] C. Hättig, J. Chem. Phys. 118 (2003) 7751.
- [23] R. Borrelli, A. Peluso, MolFC: A program for Franck-Condon integrals calculation, package available online at <http://www.theochem.unisa.it>.
- [24] R. Borrelli, A. Peluso, J. Chem. Phys. 119 (2003) 8437.
- [25] W. Domcke, G. Stock, Theory of ultrafast nonadiabatic excited-state processes and their spectroscopic detection in real time, in: Adv. Chem. Phys., Vol. 100, 1997, p. 1.
- [26] L. Edwards, D. H. Dolphin, M. Gouterman, A. D. Adler, J. Mol. Spectrosc. 38 (1971) 16.
- [27] A. Starukhin, A. Shulga, J. Waluk, Chem. Phys. Lett. 272 (1997) 405.
- [28] T. Haberle, J. Hirsch, F. Pollinger, H. Heitele, M. E. Michel-Beyerle, C. Anders, A. Dohling, C. Krieger, A. Ruckemann, H. A. Staab, J. Phys. Chem. 100 (1996) 18269.
- [29] R. S. Czernuszewicz, K. A. Macor, X. Y. Li, J. R. Kincaid, T. G. Spiro, J. Am. Chem. Soc. 111 (1989) 3860.
- [30] K. Prendergast, T. G. Spiro, J. Phys. Chem. 95 (1991) 9728.
- [31] T. Vangberg, R. Lie, A. Ghosh, J. Am. Chem. Soc. 124 (2002) 8122.
- [32] A. D. Joran, B. A. Leland, P. M. Felker, A. H. Zewail, J. J. Hopfield, P. B. Dervan, Nature 327 (1987) 508.
- [33] J. J. Hopfield, Proc. Natl. Acad. Sci. USA 71 (1974) 3640.
- [34] M. Thoss, H. Wang, Chem. Phys. Lett. 358 (2002) 298.

- [35] M. Thoss, W. Domcke, H. Wang, Chem. Phys. 296 (2004) 217.
- [36] H. Tal-Ezer, R. Kosloff, J. Chem. Phys. 81 (1984) 3967.
- [37] H. Heitele, F. Poellinger, T. Haeberle, M. E. Michel-Beyerle, H. A. Staab, J. Phys. Chem. 98 (1994) 7402.
- [38] G. Sando, K. Spears, J. Hupp, P. Ruhoff, J. Phys. Chem. A 105 (2001) 5317.
- [39] K. A. Velizhanin, H. Wang, J. Chem. Phys. 131 (2009) 094109.
- [40] D. V. Matyushov, G. A. Voth, J. Chem. Phys. 113 (2000) 5413.
- [41] R. Borrelli, A. Peluso, *submitted*.
- [42] E. Lee, E. S. Medvedev, A. A. Stuchebrukhov, J. Chem. Phys. 112 (2000) 9015.

Table 1: Frequencies, linear and second-order vibronic couplings, of five totally symmetric modes of benzoquinone. All numbers are in  $\text{cm}^{-1}$ . The high-frequency totally symmetric CH stretching modes have a negligible vibronic activity and are not reported.

Mode	$\omega_i^Q$	$\gamma_{ij}^Q$						$\kappa_i^Q$
$\nu_1$	442.28	211.4						1126.3
$\nu_2$	779.97	-20.4	433.2					168.0
$\nu_3$	1144.41	-26.5	68.7	571.9				838.8
$\nu_4$	1563.07	-25.5	-106.6	-16.9	558.6			-1785.7
$\nu_5$	1637.61	-10.2	-114.2	-7.6	-30.9	701.4		-1230.9

Figure 1: Structure of the Mg-porphyrin-benzoquinone pair as used in the electronic structure calculations. The complex has  $C_s$  symmetry.



Table 2: Frequencies and linear vibronic coupling terms  $\kappa_i^P$  of the totally symmetric modes of porphyrin. The high-frequency totally symmetric CH stretching modes have a negligible vibronic activity and are not reported.

$\omega_i^P$ (cm <sup>-1</sup> )	$\kappa_i^P$ (cm <sup>-1</sup> )
363.24	-41.0
413.23	93.7
736.22	-181.6
810.23	-397.8
1017.31	322.6
1018.25	35.0
1084.52	-92.8
1172.51	-26.8
1344.12	-32.5
1375.87	-788.2
1387.59	279.8
1461.25	-693.8
1577.95	477.4
1586.62	-545.2

Table 3: Excitation energies and diabatic coupling of the Mg-porphyrin-benzoquinone complex computed at the MCSCF/cc-pVTZ and CC2/SVP levels.

state	E(MCSCF)	E(CC2)
S <sub>1</sub> (A') (P <sup>*</sup> Q)	3.08	2.50
S <sub>1</sub> (A'') (P <sup>*</sup> Q)	-	2.50
P <sup>+</sup> Q <sup>-</sup> (A')	4.13	3.48

Figure 2: Totally symmetric normal vibrations of neutral benzoquinone and their vibrational frequencies (in wave numbers) computed at the CC2 level with the aug-cc-pVTZ basis set. The vibrational frequency of the corresponding mode of the benzonquinone anion is given in parentheses.

Figure 3: Electronic population dynamics of the ET process. The curve represents the probability of finding the system in the initial locally-excited electronic state at time  $t$ . A fast decay of the initial state population, with a time constant of about 200 fs is visible. Damped recurrences, presumably due to the reduced dimensionality of the model, are also manifest.